Note on the Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum.

By Professor H. A. Wilson, F.R.S., King's College, London.

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In a recent paper on "The Effect of Hydrogen on the Discharge of Negative Electricity from Hot Platinum,"* I gave a calculation of the thickness of the double layer on the surface and of the number of free electrons inside the platinum. Professor O. W. Richardson has pointed out to me that two terms in one of the equations, one of which I discarded as being small compared with the other, are really of the same order of magnitude. The results of the calculation are consequently wrong, and the estimate of the number of free electrons is considerably too high. The difficulty mentioned in the paper, that the energy required to raise the temperature of the electrons is apparently greater than that required to raise the temperature of the platinum, consequently disappears.

In the equation†

$$V = -\beta \log\left(1+\frac{4\pi\sigma^2}{\rho_0\beta}e^{-4\pi\sigma t/\beta}+\frac{\rho_0\beta}{16\pi\sigma^2}e^{+4\pi\sigma t/\beta}\right)$$
$$+\beta\log\left(1+\frac{4\pi\sigma^2}{\rho_0\beta}+\frac{\rho_0\beta}{16\pi\sigma^2}\right)$$

the terms $\frac{\rho_0\beta}{16\pi\sigma^2}e^{4\pi\sigma t/\beta}\,(=10^{-14})$ and 1 are quite negligible compared with $\frac{4\pi\sigma^2}{\rho_0\beta}e^{-4\pi\sigma t/\beta}\,(=10^{14})$, so that we get

$$V = -\beta\log\frac{4\pi\sigma^2}{\rho_0\beta}e^{-4\pi\sigma t/\beta}+\beta\log\left(1+\frac{4\pi\sigma^2}{\rho_0\beta}+\frac{\rho_0\beta}{16\pi\sigma^2}\right),$$

which gives, without further approximation,

$$V = 4\pi\sigma t+2\beta\log\left(1+\frac{\rho_0\beta}{8\pi\sigma^2}\right).$$

Substituting $R = NVe/J$, $Q = 4\pi\sigma teN/J$, and $\beta = \beta_0\theta$, this gives

$$R = Q+\frac{2\beta_0\theta eN}{J}\log\left(1+\frac{2\rho_0\beta_0\theta\pi t^2e^2N^2}{Q^2J^2}\right).$$

Comparing this with $R = Q+2\theta\log D/A$, we get

$$\log\frac{D}{A} = \frac{\beta_0 eN}{J}\log\left(1+\frac{2\pi\rho_0\beta_0\theta t^2e^2N^2}{Q^2J^2}\right).$$

* 'Phil. Trans.,' vol. 208, A 432.

† *Loc. cit.*, p. 270.

Now, since $p = -\rho\beta_0\theta = -ne\beta_0\theta$, we see that $-\beta_0 e\mathrm{N}$ is equal to the gas constant $\mathrm{R} = 2\mathrm{J}$; hence $\beta_0 e\mathrm{N}/\mathrm{J} = -2$. Hence

$$t^2 = \frac{Q^2\beta_0}{8\pi\rho_0\theta}\left\{\left(\frac{A}{D}\right)^{\frac{1}{2}} - 1\right\}.$$

If we take two values of Q, Q_1, and Q_2, and the corresponding values A_1 and A_2, we get

$$D = \left\{\frac{Q_1{}^2 A_1{}^{\frac{1}{2}} - Q_2{}^2 A_2{}^{\frac{1}{2}}}{Q_1{}^2 - Q_2{}^2}\right\}^2.$$

This equation, with the values found for A and Q, gives $D = 3{\cdot}7 \times 10^8$, hence $\rho_0 = -7 \times 10^{12}$. The expression for t then gives the following values:—

Q.	A.	*t*.
145,000	$1{\cdot}14 \times 10^8$	$9{\cdot}6 \times 10^{-8}$ cm.
131,000	$6{\cdot}9 \times 10^7$	9·9 ”
110,000	10^6	10·7 ”
90,000	5×10^4	9·0 ”
56,000	2×10^2	5·6 ”

The five values of t agree as well as could be expected.

Since $\rho_0 = ne$ and e is about 3×10^{-10}, we get $n = 2 \times 10^{22}$. Patterson* calculated the number of free electrons per cubic centimetre of platinum from the change in its resistance due to a magnetic field, on J. J. Thomson's theory, and got $n = 2{\cdot}8 \times 10^{22}$.

It is interesting to apply the formula for t to platinum polarised with hydrogen in dilute sulphuric acid. The potential fall in this case is about 0·9 volt, which corresponds to a value of Q about $2{\cdot}1 \times 10^4$. If, then, we suppose A/D to be small, which is the case in H_2 at high pressures, we get $t_2 = Q^2\beta_0/8\pi\rho_0\theta$, which gives, at $\theta = 300$, $t = 4{\cdot}8 \times 10^{-8}$ cm. The thickness of the double layer in this case has been estimated by several observers from the polarisation capacity and found to be about 2×10^{-8} cm.

* 'Phil. Mag.,' 6, vol. 3, p. 643.